

## REMARKS

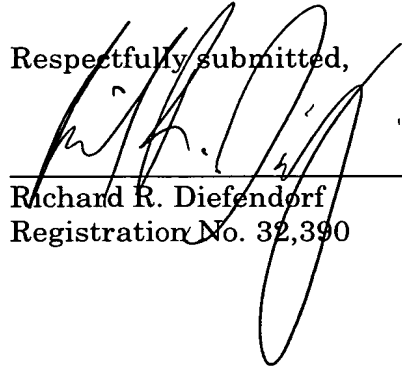
This preliminary amendment presents new claims, an amended abstract, and a substitute specification.

A marked-up version of the substitute specification, showing additions to the translation by underlining and deletions from the translation by strike through is attached Appendix III. The substitute specification includes no new matter.

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Internal Combustion Engine with Reducing Agent Generating Unit and  
Operating Method for this INTERNAL COMBUSTION ENGINE COMPRISING A  
REDUCING AGENT PRODUCTION UNIT AND OPERATING METHOD  
THEREFOR

BACKGROUND AND SUMMARY OF THE INVENTION

[0001] The invention concerns an internal combustion engine with a reducing agent-generating unit ~~with the features of the preamble of claim 1, and an operating method for this with the features of the preamble of claim 12, or an operating method with the features of the preamble of claim 13~~ the engine.

[0002] ~~The non-published~~ Non-published German patent application 10128414.4 describes an internal combustion engine with reducing agent-generating unit. The reducing agent-generating unit serves for producing an H<sub>2</sub>-containing, and NH<sub>3</sub>-containing reducing gas, which can be added upstream of an NO<sub>x</sub> catalytic converter to the exhaust gas line of the internal combustion ~~engine,~~ whereby an engine. An HC-containing (HC = hydrocarbon) fuel, as well as air and/or exhaust gas can be supplied to the reducing agent-generating unit. The generation of the H<sub>2</sub> portion, and the NH<sub>3</sub> portion in the reducing gas takes place in parallel controlled units, which makes the utilization of circuit components and the utilization of an intermediate storage unit necessary.

[0003] In contrast, ~~the~~ an objective of ~~the~~ this invention is to ~~indicate~~ provide an internal combustion engine with a reduction-generating ~~unit, and~~ unit and an operating method for this, by means of which reducing agents for effective exhaust gas cleaning can be provided in a manner simple as to construction and process engineering.

[0004] This objective is accomplished in accordance with the invention ~~by an internal combustion engine with the features of claim 1, and by a procedure with the features of claim 12.~~

[0005] The internal combustion engine of the invention ~~is characterized in that the~~ includes a reducing agent-generating unit which has an NO<sub>x</sub> generation step and an H<sub>2</sub> generation step in serial arrangement. The serial arrangement allows for a constructionally simple coupling of the generation steps with a low number of control valves, and independent of each other to a high degree, and therefore an easy to ~~be controlled~~ control operation of the generation steps. The NO<sub>x</sub> produced by the NO<sub>x</sub> generation ~~step, may~~ step may be reduced as required by reducing the H<sub>2</sub> from the H<sub>2</sub> generation step to NH<sub>3</sub>. Hereby, in connection with a suitable exhaust gas catalytic converter, an effective reducing agent for removing the nitrogen oxides present in the exhaust gas of the internal combustion engine is available. The H<sub>2</sub> produced by the H<sub>2</sub> generation step may also be utilized for the

catalytic reduction of the nitrogen oxide contents in exhaust gas, especially at low temperatures.

[0006] The H<sub>2</sub> generation step is preferably realized as a POX reactor (POX = partial oxidation). By the appropriate selection of the operating conditions of the POX reactor, the composition of the product gas may be purposefully set, so that for example a product gas rich in H<sub>2</sub>, or a product gas rich in cracked short-chain hydrocarbons is obtained. Since short-chain hydrocarbons or hydrogen are or is more effective with respect to NO<sub>x</sub> reducing than long-chain hydrocarbons, especially at low temperatures, a mineral oil used as fuel for the internal combustion engine may be turned into a more efficient reducing agent for nitrogen oxides by means of such a reactor. Furthermore, the various temperature ranges of the effectiveness of the reducing agents producible by the reducing agent-generating unit may also be utilized, and the composition of the reducing gas may be adapted to the temperature of the NO<sub>x</sub> reducing catalytic converters. An NO<sub>x</sub> reduction is thereby made possible in a wide temperature range.

[0007] The H<sub>2</sub> yield of the H<sub>2</sub> generation may be increased by including a water gas shift reaction ( $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ ), or by a steam-reforming reaction ( $\text{HC} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ ). These may also take place in the H<sub>2</sub> generation step, or in a separate a reaction step preferably downstream from the generation step. The water necessary for the run of the water gas shift reaction, or the steam reforming

reaction may be added to the relevant educt gas. If exhaust gas is added to the reducing agent-generating unit, the precondition for the run of the water gas shift reaction, or the steam reforming reaction, is already a given because of its water content.

[0008] Because of the easy oxidizability of the  $H_2$  produced by the reducing agent-generating unit, in addition a quick heating up of catalytic converters in the exhaust gas string can be achieved. By adding the produced  $H_2$  input of an exhaust gas catalyst, a rapid start-up of this catalytic converter may be achieved, which is of special importance in the reduction of pollutant emission at cold start. Similarly, catalytic converters may be effectively operated under thermally unfavorable conditions, such as in an underfloor position of a motor vehicle.

[0009] With the largely self-sufficiently operating reducing agent-generating unit, which is largely independent of the operation of the internal combustion engine, the reducing agent can thereby be made available on board of the associated motor vehicle and utilized for pollutant reduction. Since the reducing agent-generating unit can only be fed by the fuels, which are available on board of the motor vehicle anyhow, additional fuels and their storage become, or intermediate storage ~~become~~ becomes, superfluous. Furthermore, the necessity is largely eliminated of converting the operation of the internal combustion engine for providing reducing agents for the  $NO_x$  reduction, e.g. to a rich combustion, which is

associated with difficulties especially in Diesel engines. Overall, therefore, a reduction of the pollutant contents in exhaust gas is made possible in a constructionally simple manner, which is largely independent of the operation of the internal combustion engine.

[0010] In ~~the~~ a refinement of the invention, the NO<sub>x</sub> generation step is downstream from the H<sub>2</sub> generation step. This arrangement may offer benefits in the operation of the reducing agent generation. For example, the reducing gas flowing out of the upstream H<sub>2</sub> generation step in a hot state may cool down when passing through the NO<sub>x</sub> generation step, so that the subsequent components are not being stressed too much thermally.

[0011] In a further refinement of the invention, the NO<sub>x</sub> generation step is upstream of the H<sub>2</sub> generation step. This arrangement may also offer benefits in the operation of the reducing agent generation. For example, the gas flowing out of the upstream NO<sub>x</sub> generation step may be utilized for controlling the process taking place in the downstream H<sub>2</sub> generation step.

[0012] In a further refinement of the invention an NH<sub>3</sub> generation step is arranged downstream from the NO<sub>x</sub> generation step. The NH<sub>3</sub> generation step serves the on-board generation of NH<sub>3</sub>, preferably adjusted to the requirements, so

that this reducing agent does not have to be carried in a storage container for NO<sub>x</sub> reduction.

[0013] In a further refinement of the invention, a fractionating unit is arranged to the reducing agent-generating unit in such a ~~way, that~~ way that low-boiling components of a fuel used for operating the internal combustion engine are separable from the fractionating unit, which can be supplied to the H<sub>2</sub> generation step. This embodiment has the ~~advantage, that~~ advantage that a reducing agent-generating unit realized, for example, as POX reactor, is easier to operate. The low-boiling components separated from the fuel are better and more completely cracked by the POX reactor. Furthermore, the formation of soot and condensation problems in the POX reactor may largely be prevented and the operating temperatures can be reduced. The degree of efficiency and the H<sub>2</sub> yield of the partial hydrocarbon oxidation can also be improved. Furthermore, by the fractioning largely sweet fuel components may be separated. The H<sub>2</sub> generation step is therefore only supplied with low-boiling fuel components, which are free of sulphur, ~~whereby a~~ so that sulphur poisoning is minimized.

[0014] In a further refinement of the invention, the NO<sub>x</sub> generation step is operable in two operating modes with the H<sub>2</sub> generation step, such that in the first operating mode of the NO<sub>x</sub> generation step, an NO<sub>x</sub>-containing gas can be produced, and in the second operating mode an H<sub>2</sub>-containing gas and NH<sub>3</sub>-

containing gas can be produced by the reducing agent-generating unit. This refinement allows an operation of the reducing agent-generating unit advantageously according to the need. In periods of time during which the component of the reduction gas is not needed, the operation of respective generation unit may be stopped.

[0015] In a further refinement of the invention an NO<sub>x</sub> intermediate storage unit is arranged downstream from the NO<sub>x</sub> generation step. In this embodiment, the NO<sub>x</sub> generation step may also be operated with a low degree of efficiency. The NO<sub>x</sub> available only in small concentrations in the product ~~gas, is~~ gas is accumulated in the NO<sub>x</sub> intermediate storage unit, and after a certain time is available in large amounts for the reaction into NH<sub>3</sub>.

[0016] In a further refinement of the invention, the NO<sub>x</sub> intermediate storage unit is designed for the reaction of stored NO<sub>x</sub> with H<sub>2</sub> into NH<sub>3</sub>. With this double function of NO<sub>x</sub> storage and formation of NH<sub>3</sub>, the reducing agent-generating unit can have an especially compact design. In particular a NO<sub>x</sub> storage catalytic converter may be used as an intermediate NO<sub>x</sub> storage unit. An NO<sub>x</sub> storage catalytic converter optimized, for example, by an increased rhodium content, with respect to the function of NO<sub>x</sub> formation can be used within the framework of the invention.



[0017] In a further refinement of the invention, the  $H_2$  generation step is realized for the reaction of the  $NO_x$  supplied into  $NH_3$ . If the  $H_2$  generation step is simultaneously supplied with  $NO_x$  from the upstream arranged  $NO_x$  generation step, and HC-containing fuel supplied thereto, in one single, preferably catalytic operation,  $H_2$  as well as  $NH_3$  can be produced. In the partial hydrocarbon oxidation taking place under reducing conditions, the reduction of  $NO_x$  into  $NH_3$  is preferred due to thermodynamic reasons, because of which this reduction step can be put together in an advantageous fashion in one operation with the  $H_2$  generation. Thus, an  $NH_3$  and  $H_2$ -containing reducing gas is produced in one operation. Hereby, the generation of the  $NH_3$  and  $H_2$ -containing reducing gas is done preferably continuously.

[0018] In a further refinement of the invention, the  $NO_x$  generation step is designed for the generation of  $NO_x$  from air and/or oxygen-containing exhaust gas. Preferably,  $NO_x$  is produced in the  $NO_x$  generation step in a plasma process by an electric arc, or by a corona discharge. In conjunction with the downstream arranged reduction of  $NO_x$  thereby  $NH_3$  is exclusively produced from components of the air and the carried fuel, and therefore the storage of an  $NH_3$  releasing substance, such as urea, may be eliminated.

[0019] In a further refinement of the invention, the reducing  $NO_x$  catalytic converter has a denox catalytic converter step for the reaction of  $NO_x$  with  $H_2$ , and

an SCR catalytic converter step for the reaction of  $\text{NO}_x$  with  $\text{NH}_3$ . In both cases, the  $\text{NO}_x$  reduction may take place in lean exhaust gas conditions, which is the reason why the internal combustion engine is preferably operated continuously lean, and so that the full consumption benefit of the lean operation can be taken advantage of. In addition it is possible to benefit from the various temperature ranges of the efficiency of the two catalytic converter steps, which is why an efficient nitrogen oxide reduction can be achieved in a wide temperature range.

[0020] The procedure according to the invention is characterized by the following operations:

- a) Generation of an  $\text{NO}_x$  -containing gas by one of the  $\text{NO}_x$  generation steps allocated to the reducing agent generating unit from the air and/or exhaust gas supplied to the generation step;
- b) Intermediate storage of  $\text{NO}_x$  during the passage of the  $\text{NO}_x$  -containing gas produced during operation a by an  $\text{NO}_x$  intermediate storage allocated downstream to the  $\text{NO}_x$  generation step, and arranged to the reducing agent-generating unit;
- c) Generation of an  $\text{H}_2$  -containing gas by an  $\text{H}_2$  generation step allocated to the reducing agent-generating unit and arranged upstream from the  $\text{NO}_x$  intermediate storage unit from fuel, as well as air and/or exhaust gas supplied to the  $\text{H}_2$  generation step;
- d) Reaction of  $\text{NO}_x$  stored in the  $\text{NO}_x$  intermediate storage unit with the gas produced in generation step cc into  $\text{NH}_3$ , so that an  $\text{H}_2$ -containing, and an  $\text{NH}_3$ -

containing reducing gas is produced, whereby the operations a, and b are alternately performed with operations c and d.

[0021] With process control according to the invention, the  $\text{NO}_x$  generation and  $\text{NO}_x$  intermediate storage unit takes place alternately with the generation of an  $\text{H}_2$ -containing, reducing gas, release of the intermediately stored  $\text{NO}_x$  and its reduction to  $\text{NH}_3$ . An  $\text{H}_2/\text{NH}_3$ -containing reduction gas is added intermittently to the reducing catalytic converter. Since, however, preferably an  $\text{NH}_3$  storing SCR catalytic converter is employed as  $\text{NO}_x$  reducing catalytic converter, this can nevertheless continuously reduce  $\text{NO}_x$  contained in exhaust gas, since in the operating phases, in which no  $\text{NH}_3$  is added to the catalytic converter,  $\text{NH}_3$  added in the preceding operating phase and stored is used for  $\text{NO}_x$  reduction. By the  $\text{NO}_x$  intermediate storage unit in the operating phases of the  $\text{NO}_x$  generation, an enrichment of the produced  $\text{NO}_x$  takes place, which when reducing gas with reducing composition is added, is released again in higher concentration from the  $\text{NO}_x$  intermediate storage unit, and turned into  $\text{NH}_3$ . Therefore, the reducing agent  $\text{NH}_3$  can be added to the  $\text{NO}_x$  reducing catalytic converter at a comparatively high concentration.

[0022] In refinement of the procedure the  $\text{NO}_x$  reaction into  $\text{NH}_3$  takes place in an  $\text{NH}_3$  generation step, which is arranged to the reducing agent-generating unit, and arranged downstream to the  $\text{NO}_x$  intermediate storage unit. Preferably the  $\text{NH}_3$  generation step contains an  $\text{NH}_3$  formation catalytic converter which

catalyzes the reductive reaction of  $\text{NO}_x$  into  $\text{NH}_3$ . A catalytic converter with a very high efficiency with respect to  $\text{NH}_3$  ~~formation~~, is formation is for example described in the unpublished German patent application 10214686.1. If  $\text{NO}_x$  and  $\text{H}_2$ -containing reducing gas is added to such a catalytic converter, a reaction results from  $\text{NO}_x$  to  $\text{NH}_3$  from a high percentage.

[0023] In a further refinement of the procedure, the intermediate storage of  $\text{NO}_x$ , and the  $\text{NO}_x$  reaction to  $\text{NH}_3$  is performed by means of a catalytic  $\text{NO}_x$  intermediate storage. The catalytic  $\text{NO}_x$  intermediate storage preferably has an  $\text{NH}_3$  formation function in such a ~~way, that~~ way that stored  $\text{NO}_x$  is reduced to  $\text{NH}_3$  at least partially under reducing, or stoichiometrical conditions. Such a ~~behaviour~~ behavior is shown for example by  $\text{NO}_x$  storage catalytic converters, which are preferably employed here. By the functions of the  $\text{NO}_x$  intermediate storage, and the  $\text{NH}_3$  formation integrated into a catalytic component, a compact construction of the reducing agent-generating unit can be achieved.

[0024] A further procedure according to the invention is characterized by the following operations:

a) Generation of an  $\text{NO}_x$ -containing gas of an  $\text{NO}_x$  generation step allocated to the reducing agent-generating unit, from air and/or exhaust supplied to the  $\text{NO}_x$  generation step;

b) Generation of an  $H_2$ -containing and  $NH_3$  -containing reducing gas by an  $H_2$  generation step, allocated to the reducing agent-generating unit and arranged downstream from the  $NO_x$  generation step, from the  $NO_x$ -containing gas supplied to the  $H_2$  generation ~~step-operation~~ a step, fuel supplied, as well as air supplied and/or exhaust gas supplied.

[0025] By means of this process control in accordance with the invention, a continuous generation of an  $H_2$ -containing and  $NH_3$  -containing reducing gas, and its supply to the  $NO_x$  reducing catalytic converter takes place. Preferably, the  $H_2$  generation step has a catalytic converter with  $NH_3$  formation function, and by the  $H_2$  generation step an  $H_2$ -containing and  $NH_3$  -containing reducing gas is produced. The  $H_2$  elimination reaction from the HC-containing fuel in the  $H_2$  generation step, and the reduction of the added  $NO_x$  to  $NH_3$  is performed in the same procedure. Thus an  $H_2$  and  $NH_3$  -containing reducing gas is generated in one operation. This advantageously simplifies the realization of the reducing agent-generating unit.

[0026] In refinement of the procedures according to the invention in one of the fractioning units arranged to the reducing agent generation unit, a fuel enriched in low-boiling components is produced, which is added to the reducing agent generation unit for the generation of reducing gas. The  $H_2$  generation step is thereby supplied with low-molecular hydrocarbons, whereby its educt gas stream is better homogenized, a change into coke is prevented, and the  $H_2$  yield is increased.

[0027] In refinement of the procedures according to the invention the NO<sub>x</sub> reducing catalytic converter is divided into a denox catalytic converter step for the reaction of NO<sub>x</sub> with H<sub>2</sub>, and into an SCR catalytic converter step for the reaction of NO<sub>x</sub> with NH<sub>3</sub>, and depending upon its composition, the reducing gas is supplied to the exhaust gas on the input side to the SCR catalytic converter step (3a), or on the input side to the denox catalytic converter step (3b). Since the catalytic converter steps have different temperature ranges for their effectiveness, and the HC, H<sub>2</sub>, NH<sub>3</sub> generated by the reducing agent-generating unit have their optimal effectiveness at various temperatures, a high NO<sub>x</sub> reduction in exhaust gas can thereby be achieved in a broad temperature range. The denox catalytic converter step may also be designed for the reduction of NO<sub>x</sub> with HC, which expands the application area of the reducing gas.

[0028] In further refinement of the procedure, the amount and/or the composition of the reducing gas generated by the reducing gas generation unit is set as a function of the operating state of the internal combustion engine. Preferably, the reducing agent generation unit provides more reducing gas at high-volume NO<sub>x</sub> emissions of the internal combustion engine, ~~than~~ engine than at low. The procedure is preferably controlled in such a ~~way, that~~ way that the effect of the relevant NO<sub>x</sub> reducing catalytic converter brings the optimal benefit. At low charge of the internal combustion engine, or low exhaust gas temperature, preferably a

reducing gas rich in  $H_2$  is produced. At a higher load of the internal combustion engine, or a higher exhaust gas temperature, the reducing agent-generating unit is preferably operated in such a way that the reducing gas contains more  $NH_3$ . Thereby in turn an SCR catalytic converter with higher  $NO_x$  conversion is operated in the exhaust gas train of the internal combustion engine.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0029] The invention is explained below in greater detail on the basis of drawings and related ~~examples, wherein:~~ examples.

[0030] ~~Fig. 1 Is~~ Figure 1 is a schematic block diagram of an internal combustion engine with reducing agent-generating unit;

[0031] ~~Fig. 2 Is~~ Figure 2 is a schematic block diagram of a construction of a reducing agent-generating unit;

[0032] ~~Fig. 3 Is~~ Figure 3 is a schematic block diagram of the construction of a further embodiment of the reducing agent-generating unit;

[0033] ~~Fig. 4 Is~~ Figure 4 is a schematic block diagram of the construction of a further embodiment of the reducing agent-generating unit;

[0034] ~~Fig. 5 Is~~ Figure 5 is a schematic block diagram of the construction of a further embodiment of the reducing agent-generating unit; and

[0035] ~~Fig. 6 Is~~ Figure 6 is a schematic block diagram of the construction of an embodiment of the reducing agent-generating unit with an allocated fractioning unit.

#### DETAILED DESCRIPTION OF THE INVENTION

[0036] ~~In Fig.~~ Figure 1, an internal combustion engine 1 realized as a four-cylinder Diesel engine is shown here by way of example. In the following, simply the term motor will be used. The exhaust gas produced in the combustion process is conducted to the environment via the exhaust gas line 2. In exhaust gas line 2 here, by way of example the catalytic converter steps 3a, and 3b comprising the NO<sub>x</sub> reducing catalytic converter 3 is arranged.

[0037] The catalytic converter step 3a is realized as SCR catalytic converter, by means of which with NH<sub>3</sub> as reducing agent an NO<sub>x</sub> reduction takes place under lean exhaust gas conditions. An SCR catalytic converter on a V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/TiO<sub>2</sub> basis as full extrudate, or another catalytic converter suitable for the NO<sub>x</sub> reduction with NH<sub>3</sub> may be employed. The temperature range of the effectiveness of the catalytic converter step 3a normally is in the range between 200° C and 400°C.



[0038] The catalytic converter step 3b is realized as denox catalytic converter, by means of which an NO<sub>x</sub> reduction takes place under lean exhaust gas conditions with H<sub>2</sub> and/or HC as a reducing agent. Preferably a precious metal-containing catalytic converter is employed, but a Cu substituted zeolite, or another catalytic converter suitable for the NO<sub>x</sub> reduction with H<sub>2</sub> or HC may also be employed. The temperature range of the effectiveness of the catalytic converter step 3b, with H<sub>2</sub> as reducing agent, normally is in the range between 80° C and 200° C, with HC as reducing agent between 180° C and 400° C.

[0039] The reducing agent-generating unit 20 serves for the generation of the reducing agent H<sub>2</sub> and/or NH<sub>3</sub>. For this purpose, it may be supplied with fuel, or air, or exhaust gas via the fuel supply line 9, or via the gas supply line 10 as needed. The reducing agent-generating unit 20 has a controlled heating system (not shown), which is mainly operated for start-up. The reducing gas produced by the reducing agent-generating unit 20, may be added to the exhaust gas on the input side of the catalytic converter steps 3a, 3b, via the addition line 8, and the addition locations 4, 5.

[0040] The operation of the motor, and the operation of the reducing agent-generating unit 20 is controlled by a motor control unit 6, which, for this purpose is

connected with the motor 1, or with the reducing agent-generating unit 20 via control lines 7.

[0041] Of course, additional components may be arranged to the motor 1, or the exhaust gas system, which are not shown here for reasons of clear grouping. These may especially consist of further catalytic pollution abatement units, a particle filter, and sensors in the exhaust gas line 2, as well as the usual additional motor components such as injection system, exhaust gas turbocharger, components for the exhaust gas return, etc. Also not shown are switchable, or adjustable locking mechanisms in the addition line 8, and the addition lines 9, 10.

[0042] The reducing agent unit 20 is now operated in such a way that reducing gas is produced as a function of the NO<sub>x</sub> emission of the motor 1, and is added to the exhaust gas on the input side of the catalytic converter ~~steps~~ steps/step 3a and/or 3b. For this, in the motor control unit 6 ~~exists~~, there exist, for example, of performance characteristics, in which the NO<sub>x</sub> emission is laid down as a function of the motor operating point. The procedure of the reducing gas generation is controlled and monitored by the motor control unit 6, whereby the motor control unit 6 has all the necessary information available regarding the reducing gas composition, and the operating status of the reducing agent-generating unit 20.

[0043] The motor control unit 6 controls the addition amounts of air, or exhaust gas, as well as fuel, and the operation of the reducing agent-generating unit 20 preferably in such a way, that with a low exhaust gas temperature, reducing gas is mainly supplied to the exhaust gas via the addition location 4 at the inlet of the denox catalytic converter 3b. The reducing gas generation is hereby controlled in such a way, that the reducing gas predominantly contains  $H_2$  as reducing agent. Thereby, also at low exhaust gas temperatures, or at low temperatures of the catalytic converter step 3b, an efficient  $NO_x$  reduction of the motor exhaust gas is achieved. The addition amount of the reducing gas thereby is set by the motor control unit 6 according to the  $NO_x$  contents of the exhaust gas of the exhaust gas temperature, or the temperature of the catalytic converter step 3b, as well as the  $H_2$  contents of the reducing gas. Preferably a molar ratio of about 3:1 of  $H_2 : NO_x$  is set at the input side of the denox catalytic converter.

[0044] If, with increasing exhaust gas temperature, the catalytic converter step 3b falls outside of the temperature range of its efficiency, the addition amount of predominantly  $H_2$ -containing reducing gas is reduced, or stopped at the addition location 4. At the same time, the operation at the reducing agent-generating unit is changed in such a way, ~~that~~ way that this results in a higher  $NH_3$  portion, and the reducing gas is added to the exhaust gas at addition location 5 at the input of catalytic converter step 3a. Since with increasing exhaust gas temperature the SCR catalytic converter of the catalytic converter step 3a becomes gradually more

efficient, now the NO<sub>x</sub> reduction takes place predominantly at this catalytic converter.

[0045] At a further continuous increase of the exhaust gas temperature, also the SCR catalytic converter of the catalytic converter step 3a may come outside of the temperature range of its effectiveness. In this case, the reducing gas generation is changed in such a way that mainly a cracked fuel with short-chain hydrocarbons is produced from the reducing agent-generating unit 20. This reducing gas may then be conducted to the further downstream located, and therefore less hot, denox catalytic converter of catalytic converter step 3b. At this catalytic converter, at temperatures of about 300° C, an NO<sub>x</sub> reduction with these hydrocarbons takes place.

[0046] ~~It is obvious, that further~~ Further catalytic converters, which are not shown here, may be arranged in the exhaust gas line 2, which can also be supplied with reducing gas, as needed, via an appropriate addition location. In particular, H<sub>2</sub>-containing reducing gas may be apportioned to the exhaust gas at the inlet of a primary catalytic converter arranged near the motor for reducing emissions during a cold start of the motor 1. A rapid heating of the primary catalytic converter can be achieved in this way. As a consequence, pollutants can be removed from the exhaust gas already in an early phase of the motor warm-up period.

[0047] ~~Fig.~~ Figure 2 schematically shows the construction of the reducing agent-generating unit 20 in a preferred embodiment. The reducing agent-generating unit 20 here comprises an H<sub>2</sub> generation step 21, an NO<sub>x</sub> generation step 22, an NO<sub>x</sub> intermediate storage unit 23, and an NH<sub>3</sub> generation step 24 in serial arrangement. The H<sub>2</sub> generation step 21 can be supplied with fuel at measured volumes via the fuel supply line 9, and air, and/or exhaust gas via the gas supply line 10. The NO<sub>x</sub> generation step 22 can also be supplied with air, and/or exhaust gas at measured volumes via the gas supply line 10. The means used for measuring the volume are not shown here.

[0048] The embodiment of the reducing agent-generating unit 20 represented is preferably operated alternately, so that alternately NH<sub>3</sub> and/or H<sub>2</sub>, or NO<sub>x</sub> are being produced. For producing H<sub>2</sub>, the H<sub>2</sub> generation step 21 realized as a catalytic POX reactor, if needed, is first of all warmed-up to operating temperature by means of a not shown electric heater. Hereby, the operating temperature of the catalytic converter arranged in the POX reactor is about 600° C to 1000° C. Afterwards, the POX reactor is supplied with fuel, and air, or exhaust gas in a weighted flow determined by the motor control unit. Thereby, a air/fuel ratio of preferably about  $\lambda = 0.3$  is set. At this lambda value the partial fuel oxidation in the POX reactor is practically free of soot. The reaction product consists of a reducing gas with a composition, which is highly dependent on the course of procedure, i.e. mainly on the temperature of the POX catalytic converters, and on the air/fuel ratio set.

Typical content level levels of the reducing agent  $H_2$  or CO are about 18 %. The reducing gas may additionally contain a certain content of low-molecular hydrocarbons.

[0049] This reducing gas is now conducted through the  $NO_x$  generation step 22, which is not in operation during this phase of the reducing gas generation. After passing it through the  $NO_x$  generation step 22, the reducing gas flows through the  $NO_x$  intermediate storage unit 23, which contains an  $NO_x$  adsorber. The  $NO_x$  adsorber may for example be a ceramic honeycomb body, which is coated with a material, which in oxidizing conditions absorbs  $NO_x$  by adsorption, or absorption, and which releases  $NO_x$  again in reducing conditions. For this, an  $NO_x$  adsorber material on a silver basis is suitable, for example. If the  $NO_x$  intermediate storage unit was loaded with  $NO_x$  before the reducing gas produced in the  $H_2$  generation step 21 flows through, it is consequently released. The reducing gas enriched with  $NO_x$  is further conducted to the  $NH_3$  generation step 24. This preferably contains a catalytic converter with a precious metal coating. The reduction of  $NO_x$  to  $NH_3$  is catalyzed by this catalytic converter, so that finally an  $NH_3$  and  $H_2$ -containing reducing gas leaves the reducing agent-generating unit 20 via the reducing gas line 8, and is added at one, or both of the addition locations 4, 5 to the exhaust gas of the motor 1 (see ~~Fig.~~ Figure 1).

[0050] If the  $\text{NH}_3$  formation comes to a halt, for example by exhaustion of the amount of  $\text{NO}_x$  stored in the  $\text{NO}_x$  intermediate storage unit, if needed, the operation of the reducing agent-generating unit 20 for producing  $\text{NO}_x$  can be switched. For this purpose, the supply of air, or exhaust gas, as well as the supply with fuel to the  $\text{H}_2$  generation step 21 is stopped. Subsequently, the  $\text{NO}_x$  generation step 22 is supplied with air and/or oxygen-containing exhaust gas. In the  $\text{NO}_x$  generation step 22 thereupon for example a plasma process is started, or an electric arc, or a corona discharge is ignited. By such a process  $\text{NO}_x$  is produced in the nitrogen and oxygen-containing atmosphere of the  $\text{NO}_x$  generation unit. Preferably an NTP procedure (NTP = non-thermal plasma) is started, and maintained for the desired time of the  $\text{NO}_x$  generation. The  $\text{NO}_x$  produced by means of this process has a high  $\text{NO}_2$  portion of normally over 50 %, which improves the subsequent storage after the supply of the generation gas to the  $\text{NO}_x$  intermediate storage unit 23. As described above, in this situation the supplied  $\text{NO}_x$  is to be absorbed by adsorption, or by absorption. The  $\text{NO}_x$  free gas is further conducted through the  $\text{NH}_3$  generation step, from where it is added essentially unchanged to the exhaust gas of the motor 1 via the reducing gas line 8 at one of the addition locations 4, 5 (see ~~Fig.~~ Figure 1). If the  $\text{NO}_x$  intermediate storage unit 23 is saturated with  $\text{NO}_x$ , or if the supply of reducing gas to a catalytic converter step is required for other reasons, the generation of  $\text{NO}_x$  is stopped, and the generation of reducing gas with a reducing effect as described above again takes place.

[0051] ~~Fig. Figure~~ 3 schematically illustrates the construction of the reducing agent-generating unit 20 in a further preferred embodiment. The designation and the function of the of the components with the same effectiveness, corresponds to ~~Fig. Figure~~ 2. As compared to the embodiment shown in ~~Fig. Figure~~ 2, the reducing agent-generating unit 20 shown in ~~fig. Figure~~ 3 differs in the exchange of the H<sub>2</sub> generation step 21, and the NO<sub>x</sub> generation step 22. Also the embodiment of the reducing agent-generating unit shown in ~~Fig. Figure~~ 3 is preferably operated alternately such, that alternately H<sub>2</sub> and/or NH<sub>3</sub> are produced, or NO<sub>x</sub> is produced. In the operating phases with NO<sub>x</sub> generation, however, in turn the H<sub>2</sub> generation step 21 is not in operation, and the NO<sub>x</sub>-containing product gas of the NO<sub>x</sub> generation step 22 flows through the H<sub>2</sub> generation step 21. Thereby, in the warmed-up H<sub>2</sub> generation step 21 a regeneration of coking possibly caused by the cracking process may occur, which improves the operatability of the POX catalytic converter. Analogous to the function of the embodiment shown in ~~Fig. Figure~~ 2, NO<sub>x</sub> is withdrawn from the gas in the NO<sub>x</sub> intermediate storage unit 23 by storage. After switching the operation of the reducing agent-generating unit 20 by terminating the NO<sub>x</sub> generation, and starting operation of the H<sub>2</sub> generation step 21, reducing H<sub>2</sub>-containing reducing gas flows through the NO<sub>x</sub> intermediate storage unit 23, whereby the release of the stored NO<sub>x</sub> takes place, as described above. In the downstream arranged NH<sub>3</sub> generation step 24 thereupon a reaction of the stored NO<sub>x</sub> into NH<sub>3</sub> takes place, and the reducing gas is enriched with NH<sub>3</sub>.



The produced reducing gas is, as described above, fed as needed at the inlet of a catalytic converter step into the exhaust gas line.

[0052] ~~Fig. Figure~~ 4 schematically shows the construction of a reducing agent-generating unit 20 in a further preferred embodiment. Analogous to the embodiments in ~~Fig. Figure~~ 2, and ~~Fig. Figure~~ 3, this variation is also operated alternately. The differences in construction and in their function as compared to the embodiments in ~~Fig. Figures~~ 2 and 3 are described in the following. To the NO<sub>x</sub> generation step 22, here an NO<sub>x</sub> storage catalytic converter step 26 is arranged downstream, which at the same time fulfills the function of the NO<sub>x</sub> intermediate storage unit and the NH<sub>3</sub> formation. In the supply of reducing reducing gas from the H<sub>2</sub> generation step 21 to the NO<sub>x</sub> storage catalytic converter step 26, the NO<sub>x</sub> which is stored there gets released and at the same time NH<sub>3</sub> gets reduced. This effect, which occurs in the usual NO<sub>x</sub> storage catalytic converters, can be utilized advantageously. Preferably in this step 26 an NO<sub>x</sub> storage material is employed, which, with respect to the NH<sub>3</sub> formation is for example optimized by an increased rhodium content. A further simplification is achieved in that the gas necessary for the generation of NO<sub>x</sub> is supplied to the NO<sub>x</sub> generation step 22 via the H<sub>2</sub> generation step 21; therefore a branching of the gas supply line 10 can be eliminated. In comparison to the embodiments in ~~Fig. Figure~~ 2 and ~~Fig. Figure~~ 3 components can be eliminated hereby, whereby the reducing agent-generating unit 20 can be realized in a simpler way.

[0053] ~~Fig.~~ Figure 5 schematically shows the construction of the reducing agent-generating unit 20 in a further preferred embodiment. As explained in the following, this embodiment can be operated on a continuous basis, i.e. the NO<sub>x</sub> generation and NH<sub>3</sub> generation can take place simultaneously. For this purpose a reactor step 25 is provided, in which simultaneously an H<sub>2</sub> generation, preferably by a catalytic partial oxidation process, and a reduction of the NO<sub>x</sub> supplied to the NO<sub>x</sub> generation step 22, can take place. The NO<sub>x</sub> generation thereby is performed as described in the above embodiments. The necessary educt gas is supplied to the NO<sub>x</sub> generation step 22 via the gas supply line 10 as needed. The gas supply line additionally may have a branch for reactor step 25. The reactor step 25 is supplied with hydrocarbon-containing fuel via the supply line 9. Preferably in the operation of reactor step 25 an air/fuel ratio of about  $\lambda = 0.3$  is set there. In this way, the thermodynamically preferred conditions are present, on the one hand for the H<sub>2</sub> generation by partial oxidation, and on the other hand for the reduction of NO<sub>x</sub> to NH<sub>3</sub>, so that H<sub>2</sub> as well as NH<sub>3</sub> can be produced in one process. The volume ratio of these two components thereby can be set as needed by the appropriate setting of fuel, or NO<sub>x</sub> supplied to reactor step 25.

[0054] ~~Fig.~~ Figure 6 schematically shows the construction of the reducing agent-generating unit 20 in a further preferred embodiment. The reducing agent-generating unit 20 contains, analogous to the embodiment shown in ~~Fig.~~ Figure 4,

an H<sub>2</sub> generation step 21 arranged downstream to the NO<sub>x</sub> generation step 22. The furthermore downstream arranged NO<sub>x</sub> storage catalytic converter step 26 serves for the NO<sub>x</sub> intermediate storage and NH<sub>3</sub> generation. The system is preferably operated in altering generation phases, and H<sub>2</sub>, or NH<sub>3</sub> generation phases. For the generation of NO<sub>x</sub>, the NO<sub>x</sub> generation 22 is supplied with air and/or exhaust gas via the gas supply line 10. Via a branch-off, the H<sub>2</sub> generation step 21 can be supplied with air and/or exhaust gas as well. To the reducing agent-generating unit 20 furthermore a fractioning unit 27 is arranged to, in which from the fuel provided for the motor operation, low-boiling components are separated off in a fractioning process. For this purpose the fractioning unit 27 is supplied with fuel from the storage container of a motor not shown here, via the fuel supply line 9. Via the return line 9b the fuel enriched in low-boiling components is returned again. The separated low-boiling fuel components are conducted to the H<sub>2</sub> generation step 21 for H<sub>2</sub> generation via the fuel supply line 9a. By the fact, that the H<sub>2</sub> generation step 21 is operated with low-boiling hydrocarbons, the H<sub>2</sub> generation can take place with a higher yield, and the danger of coking of the POX catalytic converter is reduced. In addition, the possibility exists for preparing the low-boiling fuel components when needed only at low levels, and to add to the lean exhaust gas on the input side of a denox catalytic converter. Therefore, in the temperature range of about 200° C to 350° C an efficient NO<sub>x</sub> reduction may be achieved. To increase the H<sub>2</sub> yield in the generation of reducing gas, the reducing agent-generating unit 20 can generally be supplied with additional water. The water can thereby be taken from a storage

container of the associated motor vehicle, or be obtained by condensation from the motor exhaust gas. The water may, for example be utilized for a steam reforming process in the  $H_2$  generation step 21. Apart from the increase of the  $H_2$  content in the produced reducing gas this brings the additional advantage, that this endothermal process improves the heat and energy balance of the  $H_2$  generation. Furthermore a larger range for temperature management in the  $H_2$  generation step 21, and the complete reducing agent-generating unit 20 is gained. The water may, however, also be supplied to a water gas shift step arranged downstream from the  $H_2$  generation step 21. The thereby with  $H_2$  enriched reducing gas has a higher selectivity in the  $NH_3$  generation, and in the  $NO_x$  reduction at a denox catalytic converter. At the same time the CO contents is reduced in the reducing gas, which prevents a poisoning of the denox catalytic converter by CO accumulation of active catalytic centers.

[0055] It is obvious that to the reducing agent-generating unit 20 heat exchangers may be arranged to, in order to improve the heat and energy balance of the total process, and the course of the procedure. Thus, for preheating of the supplied air, or the supplied exhaust gas for example, a heat exchanger may be provided in the gas supply line 10. Heat exchangers may, however, also be provided in the reducing agent-generating unit 20, for example in order to utilize the heat content of the hot product gas flow of the  $H_2$  generation step, or the  $NH_3$  generation step for preheating of the educt gas of a preliminary step.

Summary ABSTRACT OF THE DISCLOSURE

~~1. Internal combustion engine with reducing agent generating unit and operation method for this.~~ 2.1. An internal combustion engine with a reducing agent-generating unit (20) for the generation of an H<sub>2</sub>-containing and/or NH<sub>3</sub>-containing reducing gas, which can be added to the an exhaust gas line (2) upstream from an NO<sub>x</sub> reducing catalytic converter (3) ~~is proposed, as well as, and~~ a procedure for the operation of such an internal combustion engine are proposed. 2.2. ~~According to the invention, the~~ The reducing agent-generating unit (20) ~~consists of~~ has an NO<sub>x</sub> generation step and an H<sub>2</sub> generation step in serial arrangement. ~~For the procedure, it is provided that, at least temporarily,~~ NH<sub>3</sub> is formed at least temporarily by chemical reaction by the reducing agent-generating unit (20) from NO<sub>x</sub> produced in the NO<sub>x</sub> generation step. 2.3. ~~Application~~ The invention is applicable in motor vehicles, especially in passenger vehicles with Diesel engines.

3. ~~Fig. 1~~